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SYNTHESIS, CHARACTERIZATION AND COMPUTATION OF POTASSIUM DOPED CALCIUM HYDROXIDE NANOPARTICLES AND NANOTUBES

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ABSTRACT

Potassium doped calcium hydroxide [Ca(OH)2:K] nanoparticles were synthesized by simple precipitation method. The powder x-ray diffraction pattern of the sample was studied, to investigate the crystalline nature of the sample. The shape and size of the nanoparticles were measured by scanning electron microscopic (SEM). The functional groups presented in the synthesized particles were recorded and analysed in the spectral region of 4000-400cm^{-1}by Fourier-transform infrared spectroscopy. Optical Properties of [Ca(OH)2:K] were determined by ultraviolet visible spectrometer in the range of 190 – 800 nm. In addition that to study insight of the Ca(OH)2 nano material, a nanotube was constructed and studied a quantum chemical calculations to predict the geometry, Dynamic and band gap properties.

KEYWORDS: Potassium Doped Calcium Hydroxide; Structural Properties & Optical Properties

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Original Article

INTRODUCTION

In recent years, a widespread research has been made on calcium hydroxide (Ca(OH)2) nanoparticle (NP), since it has a vital applications various fields. Ca(OH)2 NPs has numerous applications such as paper de-acidification, wall painting, consolidation of artwork, natural stones, wood, cultural heritage conservation [1-5], CO_2 adsorption of greenhouse gas and endodontic [6-8]. Since it has potential applications, we are interested in investigating the optical behaviour of Ca(OH)2 when doped with potassium (K). In the present study, we synthesize potassium-doped Calcium hydroxide (Ca(OH)2:K) nanoparticle and characterize the structure, optical band gap and surface morphology (SEM). In addition to that using quantum chemical, DFT and Td-DFT method of calculations a Ca(OH)2 nanotube was studied, it provides as detailed information about geometry, band gap and a vibration picture of the Ca(OH)2 NPs. Besides that to investigate the functional groups and optical gap the FT-IR spectrum and optical absorbance UV-Visible spectrum was recorded.

EXPERIMENTAL DETAILS

Materials and Methods

Chemicals and reagents were used in this study were analytical grade and used without further Purification. Calcium chloride ($CaCl_2$, Merck), Sodium hydroxide (Na(OH), Merck), Potassium Chloride (KCl, Merck) were used as starting materials.

Synthesis of Potassium Doped Calcium Hydroxide

The $Ca(OH)_2$ doped with K doped nanoparticles were synthesized by the following reaction:

$CaCl_2+2NaOH+KCl \rightarrow Ca(OH)_2$ K+ 2NaCl

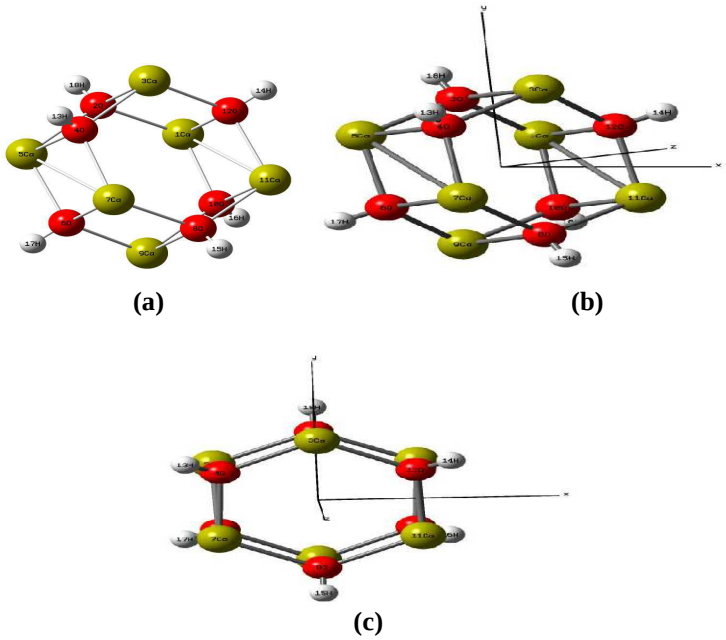
$CaCl_2$, 3.3g and NaOH, 2.4g was dissolved in 100 ml of double distilled water and stirred for 15 min. At 70°C to obtain a clear solution, the cyclohexane was added into the prepared clear solution and maintained in a beaker. In the meantime, 0.7 g of potassium chloride was dissolved in 20 ml of distilled water and added into the beaker by drop wise under vigorous stirring. The mixture was maintained at the standard temperature. The mixture was centrifuged and washed with water, then dried at 60°C using the micro oven. Finally, the white colour powder was obtained.

Characterization and Instrumentation

The potassium doped calcium hydroxide was studied using powder x-ray diffraction method. Ca(OH)2:K was dissolved in de-ionized water, and its optical behaviour was examined bya UV spectrophotometer (systronics) (Perkin-Elmer lambda 25 UV spectrometer). The Fourier-transform infrared spectrum (FTIR) of the powdered solution was recorded in KBr medium in the range of 400-4000 cm^{-1}using Perkin Elmer RX1 infrared scanner. The morphology, size distribution, and shape of the prepared nanoparticles were observed by scanning Electron Microscopy (SEM).

Computational Details

Complementary density functional theory (DFT) and Time-dependent DFT calculations were performed using Gaussian 03 program [9, 10]. The B3LYP/LANL2DZ basis was used to calculate the molecular geometry, vibrational frequencies, and electronic excitations. Initially, a minimum size of Ca(OH)2 nanotube was constructed in the range about 0.344 nm of breadth and 0.666 nm of length. The nanotube consists of 6:6 ratio oxygen and calcium hydroxide atoms in Hexagonal shape [11]. The optimized structure of NT of Ca(OH)2 is shown in Figure 1.



(a) **(b)**

(c)

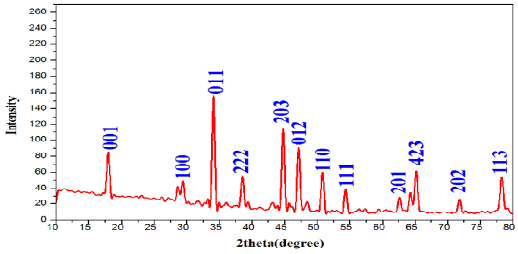
Figure 1: The Optimized Ca(OH)2 nanotube(3,3) by B3LYP/LANLD2Z Basis Seta) The Hexagonal Shape of NPs, b) Vertical View of the NPs c) NPs is Horizontal View

RESULTS AND DISCUSSION

The geometry calculation of $Ca(OH)_2$ nanotube performed with the hexagonal packing system. Atomic bonding appears as Ca-O, Ca-Ca, and O-H, its bond lengths calculated in angstrom (Å). The bond length of $Ca1\text{-}O_2$ is about 2.425Å whereas $Ca3\text{-}O_4$ and $Ca3\text{-}O_{12}$ have slightly lesser (2.368 and 2.369Å) than that, it is due to the positioning of atoms, the $Ca1\text{-}O_2$ is a bonding between the hexagon and whereas the counterpart is within the hexogen. On the whole, Ca-O has a lesser bond length along the line joining position in the nanotube. The Ca-Ca bonding was calculated higher than Ca-O bond lengths about 4.229Å caused its interaction due to inter-bonding between ortho and para-positioned atoms. The optimized bond parameters are presented in Table 1.

Table 1: The Optimized Bond Parameters Of Ca(OH)2 Nanotube, Using B3LYP/LANL2DZ Basis Set

Parameters Bond Length (Å)		Parameters Bond Length (Å)		Parameters Bond Length (Å)	
Ca-O		Ca-Ca		O-H	
Ca1-O2	2.425	Ca1- Ca3	3.697	O2-H18	0.985
Ca1-O12	2.391	Ca1-Ca5	4.229	O4-H13	0.987
O2- Ca3	2.451	Ca1-Ca9	4.097	O6-H17	0.987
O2- Ca5	2.425	Ca1-Ca11	3.634	O8-H15	0.985
Ca 3-O4	2.368	Ca3- Ca5	3.698	O10-H16	0.987
Ca3-O12	2.369	Ca3-Ca7	4.093	O12-H14	0.987
O4- Ca5	2.391	Ca3-Ca11	4.095		
Ca5- O6	2.390	Ca5-Ca7	3.635		
O6-Ca7	2.391	Ca5-Ca9	4.093		
Ca7-O8	2.425	Ca7-Ca9	3.697		
O8-Ca9	2.451	Ca7-Ca11	4.229		
Ca9-O10	2.368	Ca9-Ca11	3.697		
O10-Ca11	2.391				
Ca11-O12	2.390				



(a): The Powder X-Ray Pattern of Ca(OH)2 : K

(b) The White Colored Powder Sample of Ca(OH)2 nanoparticles

Figure 2: The Powder X-ray Pattern and Synthesized Sample of Ca(OH)2:K

The XRD pattern and the synthesized sample have shown in Figure 2. The pattern indicates that the crystalline nature and miller indices of Ca(OH)2, appeared as (001), (100), (110) and (111), it confirms the indexed hexagonal structure Ca(OH)2 [12, 13], the 2θ degrees appears at 18.13, 29.49, 50.82, and 54.33. The Potassium doping in Ca(OH)2 was confirmed, due to the presence of miller indices (011), (222) and (202) at a 2θ angle of 34.10, 38.52 and 71.94 respectively. The SEM image of pure potassium doped calcium hydroxide nanoparticles shows hierarchical nanostructure of flower-like morphology with a mean diameter of 2μm, which consist flower and rod-shaped nanostructures as shown in Figure 3.

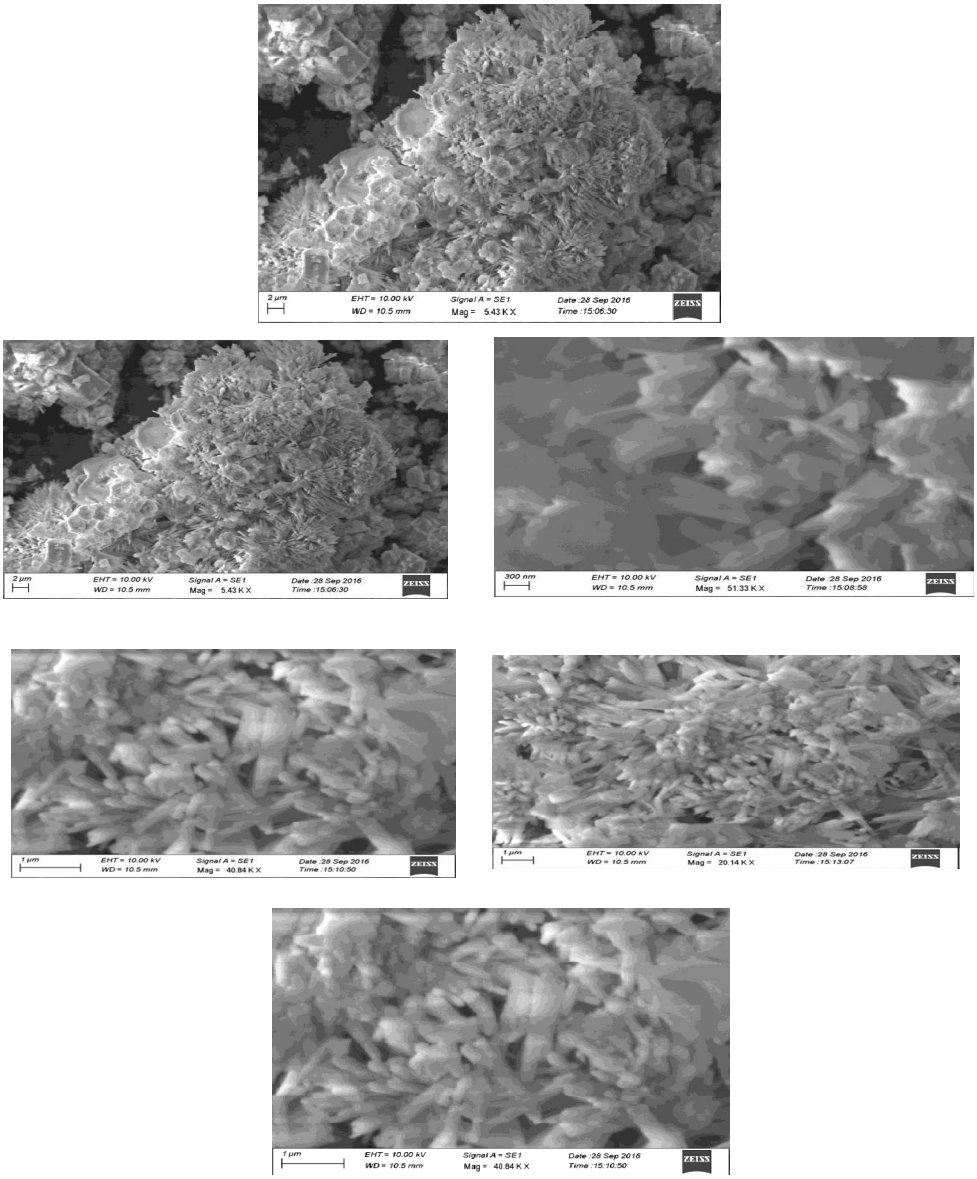


Figure 3: SEM Analysis of Potassium Doped Ca(OH)2 nanoparticles

It is exactly matched with traditional Ca(OH)2 nanoparticles structure [12 14]. The Ca(OH)2 NPs has a hexagonal shape with several nanometers in thickness (40-45nm) and breath (600-650nm) [14]. In the present investigation, we obtained an exact sign of Ca(OH)2:K NPs in different magnification. Further FT-IR spectrum was recorded (as shown in Figure 4)

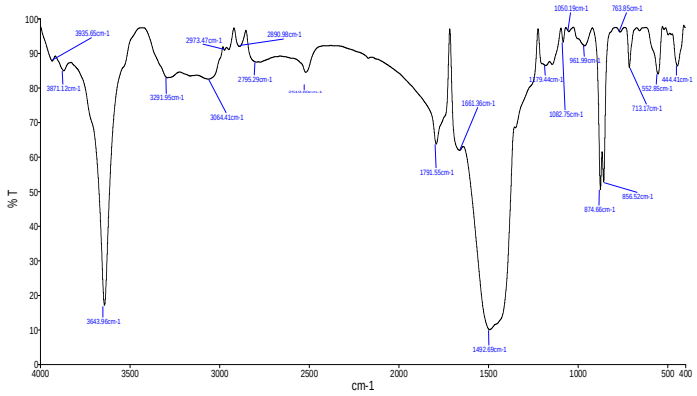


Figure 4: The Experimental FT-IR Spectrum of Ca(OH)2:K

To find the presence of functional groups in the range of 4000-400cm^{-1}, the vibrational picture of the Ca(OH)2: K NPs sample shows a peak at 3643.96 cm^{-1}belongs to O-H stretching band as a sharp peak [12]. A counterpart computed wave numbers appear at 3498 and 3456 cm^{-1}, it shows a deviation (145 and 187 cm-1) due to the chemical environment. The peak at 1661 cm^{-1}indicates the bending of the O-H band, this peak shows a small difference from the literature [12], it is due to the Potassium element presented in the material. A peak appeared at 875 cm^{-1}is belongs to CaO_3, as a strong band with a double peak of 857 cm^{-1}. Also, a medium intensity peak of CaO stretching has obtained at 444 cm^{-1}, whereas the calculated wave number of the same mode has obtained at 359cm^{-1}. The wagging in plan bending vibration of Ca(OH)2 has appeared at 553 cm^{-1}, its corresponding computed values is about 564 cm^{-1}, it shows good agreement among both the methods. The recorded and computed wave numbers were presented in Table 2. The computed wave numbers were scaled down by 0.961 to bring the computed results near with observed Values as suggested by CCCBDB [15].

Table 2: The FT-IR and B3LYP/LANL2DZ Basis Computed Wave Number of $Ca(OH)_2$:K and Computed $Ca(OH)_2$ NTS (Scale Factor: 0.961)

Un Scaled (cm^{-1})	Scaled (cm^{-1})	FT-IR (cm^{-1})	Assignments
373.58	359	444	νCaO
559	537		ωCaOH
586.61	564	553	ωCaOH
714.91	687	713.17	tCaOH
3596.39	3456		νOH
3639.64	3498		νOH
3640.33	3498	3643.96	νOH

The UV absorption spectrum was recorded in the range of 190-1100 nm and its shown in Figure 5, there is a peak appeared at 235 nm due to the absorption of $Ca(OH)_2$:K nanoparticles. The peak has emerged in the conjugative range of π-π* transition and it reflects the optical behaviour of the material. On the other hand, the predicted Td-B3LYP calculation the band gap of Ca(OH)2 NT is calculated about -0.4696eV. It is the difference between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), HOMO has appeared over the ortho-meta position of the hexagonal and LUMO located over the Para position of the hexagon. The closer band gap among HOMO and LUMO indicates the ability to react with a substituent. This kind of materials is very suitable for Endodontic [8]. The frontier molecular structure of HOMO-LUMO has shown in Figure 6

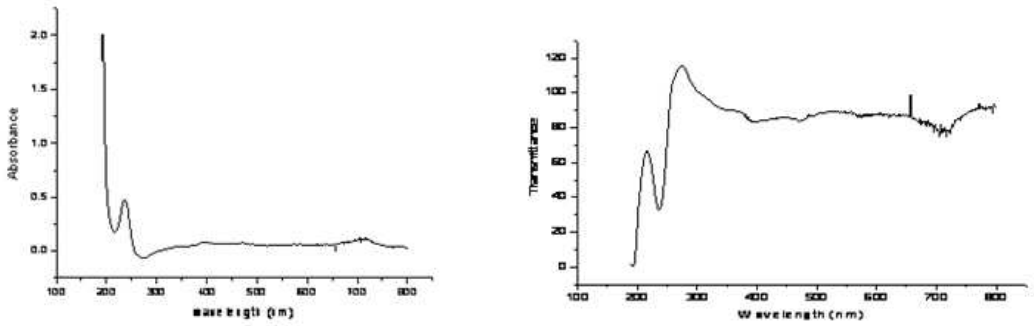


Figure 5: UV Absorbance and Transmittance of Potassium Doped Ca(OH)2 nanoparticles

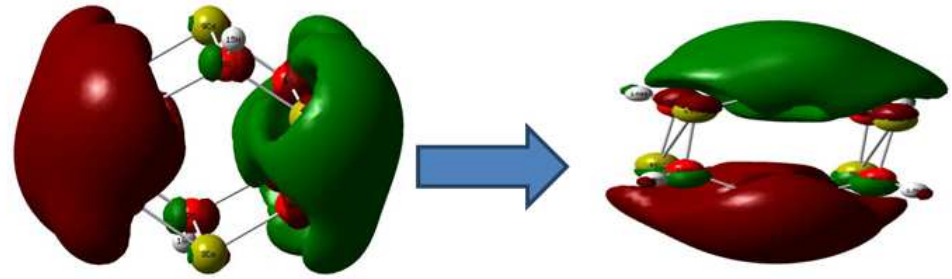


Figure 6: The Frontier Molecular Orbital's of Ca(OH)2 NT Using Td-DFT Calculation

CONCLUSIONS

The potassium doped Calcium hydroxide nanoparticles were prepared using the wet chemical method. The atomic plane was found using powder X-ray diffraction method, miller indices of Ca(OH)2: K were (001), (100), (110), (111), (011), (222) and (202). The SEM image analysis confirmed the flower and rod shape morphology of the potassium doped calcium hydroxide nanoparticles with 2µm diameter. In FTIR, the typical hydroxyl group and Ca-O stretching, and Ca-O-Ca bending vibrations were found at a characteristic region. The UV-Visible spectrum dealt the optical behaviour of NPs and NTs, absorbed optical gap is in the conjugative region (235nm), where exist π-π* transition between p and d orbital electrons. The calculated band gap of NT is about -0.4696 eV, shows a good sign of reactivity of the material.

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